Final Report

Title: The Oxidation of Arsenic (III) and Antimony (III)

Principal Investigator: John G. Mason
Department of Chemistry
Virginia Polytechnic Institute
Blacksburg, Virginia   24061

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Abstract

The oxidation of As(III) by Cr(VI) has been studied in detail for a variety of systems. In acetic acid-acetate buffers and aqueous acetic acid the rate law obtained is of the general form:

$$-\frac{d[Cr(VI)]}{dt} = \frac{(k_o + k_1[HOAc])K[As(III)][Cr(VI)]}{1 + K[As(III)]}$$

Numerical values of K and k_o are the same for both systems, but the coefficient for the acetic acid catalyzed system is different. The mechanism suggested by the rate law is

$$As(III) + HCrO_4^- \rightleftharpoons [As(III) \cdot HCrO_4^-] \quad K$$
$$[As(III) \cdot HCrO_4^-] \xrightarrow{k} products$$
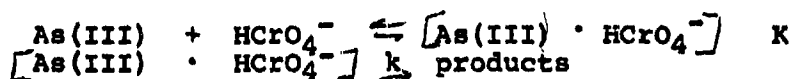
The decomposition of the mixed anhydride is acid-catalyzed.

In dilute perchloric acid solution, the rate law found was

$$-\frac{d[Cr(VI)]}{dt} = \frac{(k_o + k_1[H^+] + k_2[H^+]^2)K[As(III)][Cr(VI)]}{1 + K[As(III)]}$$

The interpretation here is essentially the same since k_o and K have approximately the same values as before. The two term hydrogen ion dependence is taken to be the protonation of the mixed anhydride.

In hydrogen phosphate ($HPO_4^=$) – dihydrogen phosphate ($H_2PO_4^-$) buffers, a different mechanism is operative. The reaction appears to be simple first order in As(III) and first order in Cr(VI). The Cr(VI) complexes with the buffer components and analysis of the data shows the most significant activated complex to have the composition ($HCrO_4^- \cdot HPO_4^=$) or ($CrO_4^= \cdot H_2PO_4^-$). The

most significant solution complex was found to be $HCrO_4^- + H_2PO_4^-$ $\rightleftharpoons HCrPO_7^= + H_2O$. No evidence for As(III)-Cr(VI) association was found in NH_4NO_3-KNO_3 media.

The primary reaction between As(III) and Cr(VI) was found to induce the oxidation of tartaric acid producing a catalytic rate enhancement. Detailed kinetic studies showed that the catalysis was pH dependent in acetic acid-acetate buffers in contrast to the primary reaction and that the most reasonable reactant was the monoanion of tartaric acid. Tartaric acid was found incorporated in the reduction product of Cr(VI). Essentially the same spectrum was produced by heating Cr(III) with tartaric acid as by reduction of Cr(VI) in tartrate medium. The kinetics thus far have been too complex for simple interpretation. Oxalate ion also exhibited a "catalytic" effect on the disappearance of Cr(VI), presumably by induced oxidation.

The reaction of Cr(VI) with antimony tartrate was much too rapid to measure. However, essentially the same observations with respect to both the stoichiometry and to the nature of the Cr(III) product were made.

FINAL REPORT

Personnel:

For the period covered, the research personnel consisted
of John G. Mason, Principal Investigator, A. D. Kowalak, and
P. T. Chang, Research Assistants, and R. M. Tuggle, part-time
technician summer 1965 and academic year 1966. Dr. Kowalak
terminated in June 1965 having completed the doctorate. Mr.
Chang was terminated without degree, December, 1967.

Scope and Objectives:

The original objective was to investigate the kinetics
and mechanisms of the oxidation of arsenic(III) and antimony
(III) by chromium (VI) and cerium(IV). Further, it was hoped
to investigate the catalysis of these reactions with a view to
(1) clarification of the mechanisms and (2) possible analytical
applications. Work was initiated with the detailed study of
the Cr(VI)-As(III) in acetic acid-acetate buffer solutions.
Detailed studies were made in acetic acid-acetate buffer
solutions, acetic acid solutions, dilute acid solutions, and
dihydrogen phosphate-mono-hydrogen phosphate buffer systems.
This work has been prepared for submission and copies of the
two manuscripts so prepared are appended to this report as
attachments. The studies of utilizing cerium(IV) were incor-
porated into the Ph.D. program of Mr. Ping-Tzu Chang. Unfort-
unately, only a few measurements were performed due to the
early termination of Mr. Chang.

Accomplishments:

The work accomplished will be summarized according to the reactions studied.

The Chromium(VI)-Arsenic(III) Reaction.

This reaction was studied in considerable detail under a variety of conditions. Since the initial work has been published (J. G. Mason and A. D. Kowalak, Inorg. Chem. 1964) and the rest is incorporated in the attached manuscripts, only a brief summary will be made here.

The primary reaction of Cr(VI) with As(III) was found to have the expected stoichiometry in outgassed solutions

$$2 \, Cr(VI) + 3As(III) = 2 \, Cr(III) + 3 \, As(V).$$

In acetic acid-acetate buffers, the rate of the disappearance of Cr(VI) was found to be essentially pH independent and to obey the following rate law

$$\frac{-d[Cr(VI)]}{dt} = \frac{(k_o + k_{HOAc}[HOAc])K[As(III)][Cr(VI)]}{1 + K[As(III)]} \, .$$

In solutions of high Cr(VI), where the reactions were studied titrimetrically by following the As(III) the following rate law was obtained.

$$\frac{-d[Cr(VI)]}{dt} = \frac{(k_o + [k_{HOAc}[HOAc]])K[As(III)][Cr(VI)]}{1 + K[As(III)]} +$$

$$(k_o' + k_{HOAc}'[HOAc])[As(III)][Cr_2O_7^=]$$
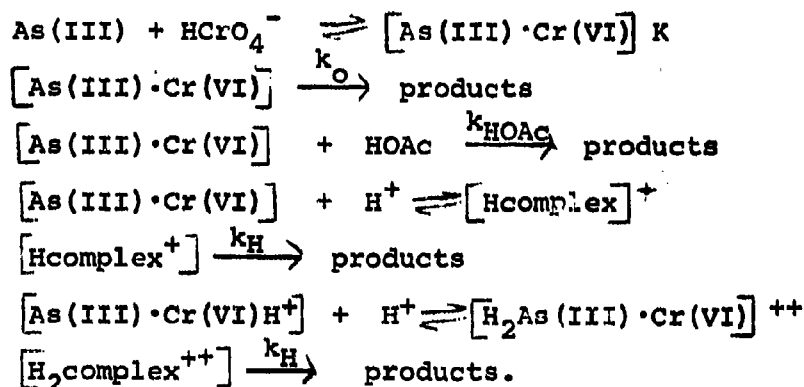
For solutions of dilute acetic acid

$$\frac{-d[Cr(VI)]}{dt} = \frac{(k_o + k_{HOAc} \text{ "} [HOAc])K[As(III)][Cr(VI)]}{1 + K[As(III)]}$$

For solutions containing low concentrations of perchloric acid

$$\frac{-d[Cr(VI)]}{dt} = \frac{(k_o + k_H[H^+] + k[H^+]^2)K[As(III)][Cr(VI)]}{1 + K[As(III)]}$$

The mechanism proposed to rationalize these results is in essence the following:

$$As(III) + HCrO_4^- \rightleftharpoons [As(III) \cdot Cr(VI)]^- \quad K$$
$$[As(III) \cdot Cr(VI)]^- \xrightarrow{k_o} products$$
$$[As(III) \cdot Cr(VI)]^- + HOAc \xrightarrow{k_{HOAc}} products$$
$$[As(III) \cdot Cr(VI)]^- + H^+ \rightleftharpoons [Hcomplex]^+$$
$$[Hcomplex^+] \xrightarrow{k_H} products$$
$$[As(III) \cdot Cr(VI)H^+] + H^+ \rightleftharpoons [H_2As(III) \cdot Cr(VI)]^{++}$$
$$[H_2complex^{++}] \xrightarrow{k_H} products.$$

Values of K found in all acid media were essentially the same, approximately 17. The only significant anomaly lies in the fact that k (which is also constant in acid solution) is not numerically equal to the value of k_o in NH_4NO_3 solutions. However, no retardation by As(III) was observed so that the same mechanism is not operative. It appears that if a sufficiently strong acid is present, the equilibrium reaction is not rate determining. In the absence of an acid of sufficient strength, the rate determining step is the formation of the

activated complex without the pre-equilibrium step. The catalytic coefficient for acetic acid catalysis likewise is numerically different and a function of the acetic acid concentration and/or hydrogen ion. Contrary to published reports we observed spectral changes in the acetic acid solutions which suggest that Cr(VI) and acetic acid complexation occurs which could account for the more profound effect of acetic acid in the absence of acetate. There is also the possibility that in the acetate-acetic acid solutions homoconjugation occurs to produce the species $H(OAc)_2^-$ and alter the catalytic properties of the solutions.

The Cr(VI)-As(III) Reaction in $H_2PO_4^- $-$HPO_4^=$ Buffers.

The reaction was found to proceed via a very complex path. The principal results found are these:

(1) Acid chromate ($HCrO_4^-$) forms a complex with $H_2PO_4^-$ which is kinetically active. Spectral evidence was in accord with the kinetics.

(2) The most kinetically active form however, has the composition $HCrO_4^- \cdot HPO_4^=$ or $CrO_4^= \cdot H_2PO_4^-$. No physical evidence was found for its existence in finite quantities.

(3) Serious salt effects were observed and detailed corrections were attempted.

(4) No retardation at high As(III) was observed; the reaction remaining second order without complications due to As(III).

(5) The final form of the rate law is

$$\frac{-d[Cr(VI)]}{dt} = \left\{\frac{k_1[HCrO_4^-][H_2PO_4^-] + k_2[CrO_4^=][H_2PO_4^=][As(III)]}{1 + K[H_2PO_4^-][HCrO_4^-]}\right.$$

In no case was evidence found for the presence of As(IV).

The Cr(VI)-As(III) Reaction--Kinetic Anomalies

In attempts to reproduce independently our previous results on the Cr(VI)-As(III) reaction anomalous results were obtained when low As(III) concentrations were tried. These anomalies were reflected in the log $(A_t - A_\infty)$ vs. time plots which were composed of two linear segments. In most cases at long times the rate constant evaluated from the second segment was identical with the previously established value. However the initial portion was much faster than the normal or expected rate. A detailed investigation was instituted to discover the source of this anomaly. Ultimately it was discovered that the anomalous results were due to the stirring rate while the solutions were being mixed. Extremely efficient mixing produced normal behavior while a somewhat slower degree of mixing produced a perfectly homogeneous system but the kinetic behavior was different. These differences are illustrated in Fig. 1.

For the evaluation of the data several logical restrictions were placed upon the data selected as follows:

(1) the zero time value of the absorbance should correspond to the initial absorbance calculated from the Beer's Law plot for the initial Cr(VI) concentration.
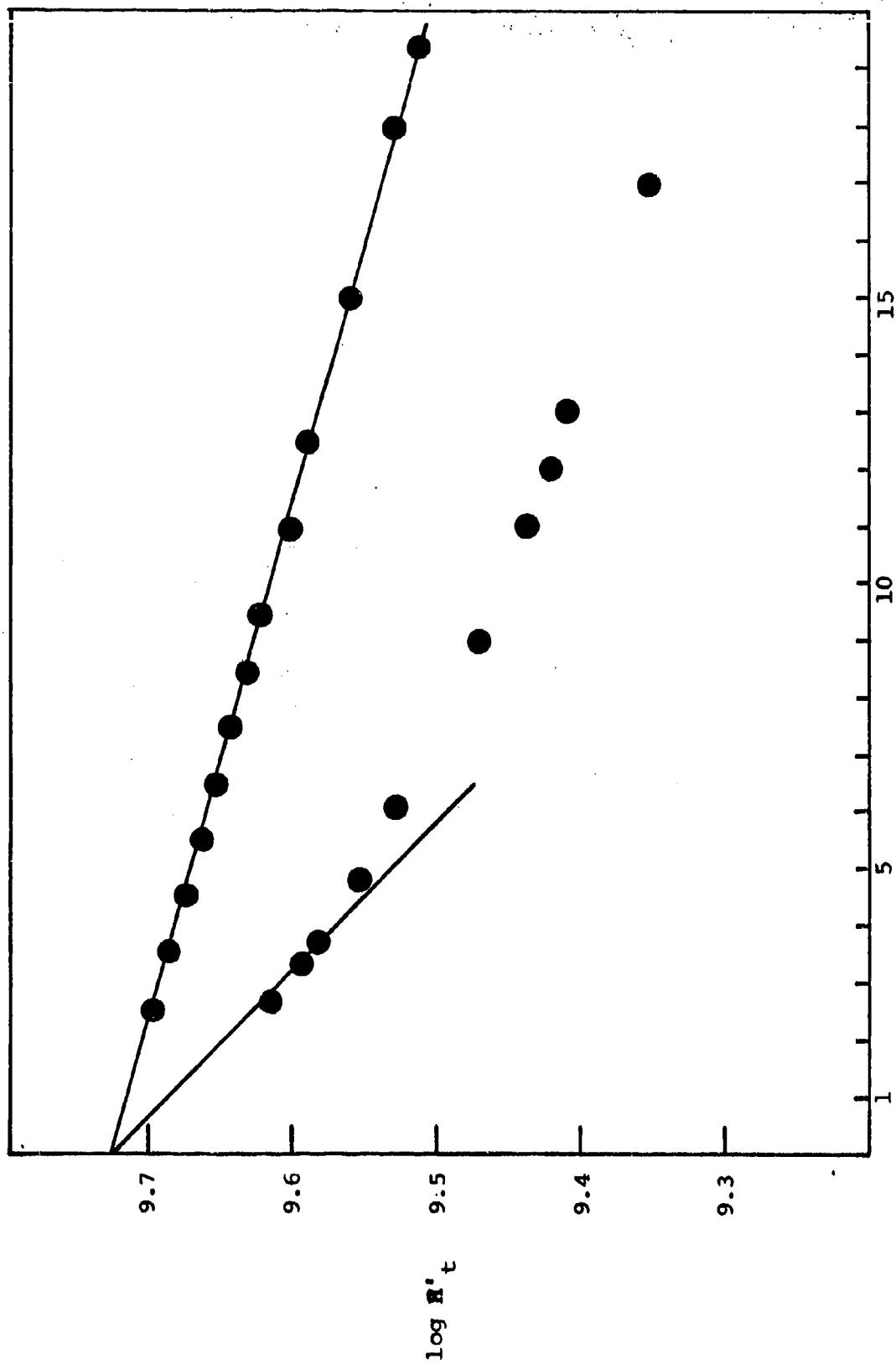
FIGURE 1

(2) the reaction should attain the appropriate steady
   state at long times.

These restrictions were placed upon the data to insure that
the reaction mixture was truly homogeneous after mixing and
only the method of initial addition produced the effect and
that conditions were such that the true steady state region
was achieved.

In order to analyze the selected data, the first step
was to evaluate the initial rate constant for the disappearance
of Cr(VI). These data are tabulated in Table 1. The initial
rate of disappearance of Cr(VI) in the cases tried showed values
for the initial rate of 7.9×10^{-4} sec^{-1} or lower. For compar-
ison the steady state rate constants are k = 7.5×10^{-4} and
$kK[As(III)]$ = 3.36×10^{-4}. If the interpretation is made that
complex formation occurs without oxidation, i.e., complex
formation is a non-productive path, then the product $kK[As(III)]$
is the pseudo first order rate constant for the formation of
the activated complex. The initial rates are considerably
higher than this value and remarkably close to the estimate
of the decomposition of the complex. This suggests that the
technique of mixing leads to an overproduction of the complex,
that is, a concentration in excess of the steady state. Using
this assumption it was possible to analyze the data according
to the mathematical procedure of Alberty and Miller [J. Chem.
Phys., 26, 1231 (1957)], who derived the detailed concentration

Table I
Initial Rates
$$[As(III)] = 2x10^{-2}$$

$[HCrO_4^-] \times 10^4$	Initial $k \times 10^4$
1.04	7.4
1.04	8.3
1.55	6.2
2.33	8.3
3.1	5.2
3.1	7.6
6.2	4.49
6.2	5.52

Ionic strength 1.5M adjusted with KNO_3
$T = 25^{\circ}C$.   0.2M KOAc - 0.2M HOAc Buffer.

time profile for the mechanism

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \overset{k_3}{\longrightarrow} C$$
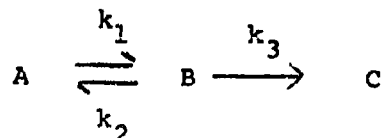
In final form their results are

$$A = xe^{m_1 t} - ye^{m_2 t}$$

$$B = \frac{(m_1 + k_1)xe^{m_1 t}}{k_2} - \frac{(m_2 + k_1)\,ye^{m_2 t}}{k_2}$$

where
$$x = \frac{k_2 B_O - (m_1 + k_1)A_O}{m_1 - m_2}$$

$$y = \frac{k_2 B_O - (m_1 + k_1)A_O}{m_1 - m_2}$$

$$m_1 = \frac{1}{2}\left[-(k_1 + k_2 + k_3) - \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3}\,\right]$$

$$m_2 = \frac{1}{2}\left[-(k_1 + k_2 + k_3) + \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3}\,\right]$$

It is necessary to know A_O and B_O in order to calculate the concentration-time curve. Further all previous work indicated that the complex and uncomplexed Cr(VI) had essentially the same absorption spectrum. Therefore to analyze the data required that A + B at time t be known. To check on the assumption that what was being measured spectrophotometrically was in fact total Cr(VI), atypical runs for the same conditions which produced curvature were analyzed by a different method. Individual samples were taken during the run, quenched with

base, and quickly analyzed for $CrO_4^=$. The $\boxed{Cr(VI)}$ -time
curve obtained in this way is different in no essential way
from that obtained by the normal method.

Values of A_o and B_o were made on the assumption that only
B_o lead to product, hence the initial rate was a measure of
B_o; A_o was then calculated by material balance. On this basis
the values of k_1, k_2, and k_3 were determined.

$$k_1 = 7.4 \times 10^{-4} \text{ sec}^{-1}$$
$$k_2 = 9.8 \times 10^{-4} \text{ sec}^{-1}$$
$$k_3 = 7.5 \times 10^{-4} \text{ sec}^{-1}$$

The agreement between calculated and measured absorbances was
within 10%. The reaction is quite complex involving acid
catalysis terms so that detailed analysis is not possible.
However, these data support the argument that oxidation occurs
via the complex rather than the direct oxidation.

The Cr(VI)-Sb(III) Reaction.

Under all conditions tried comparable to those which
were used for the analogous reaction with arsenic(III), the
reaction rate was found to be too rapid for convenient study.
However, the solubility of Sb_2O_3 was so low that attempts were
made to improve the solubility by complexation. The complexing
agent selected was tartaric acid. Initial investigations of the
stoichiometry of the Sb(III)-Cr(VI) reaction in tartrate con-
taining solutions indicated a dependence upon tartrate suggest-
ing the induced oxidation of tartaric acid had occurred. This
was later confirmed and will be discussed in the following
section.

Since the reaction of Cr(VI) with As(III) had been thoroughly
studied it was decided to study the effect of tartrate on the
Cr(VI)-As(III) reaction.

The Cr(VI)-As(III) Reaction in the Presence of Tartaric Acid.

A. Stoichiometry. The stoichiometry was studied under
essentially the same conditions as the kinetic measurements.
An excess of As(III) was used and the stoichiometry studied as
a function of the tartaric acid. The reaction was allowed to
reach completion by standing for three days. The buffers used
were 0.2M KOAc-0.2M HOAc adjusted to 1.5M ionic strength with
KNO_3. The excess of As(III) was determined by titration with
standard I_2. The initial attempts produced rather curious results:
(1) the initial color of the solution was red-purple, adjustment

of the pH to 10 followed by titration with I_2 showed a progressive change in color as the titration proceeded the expected green of the Cr(III) product in this solution being formed. (2) End point location was found to be impossible because a slow reaction consuming I_2 was found to be proceeding in the vicinity of a rational end point. Titration at ice-temperatures did not eliminate the progressive fading of the end point. (3) The addition of excess I_2 followed by back titration with standard As(III), produced as a total slightly more equivalents of As(III) than were originally present.

These results suggested that an oxidation product of tartaric acid was either coordinated with Cr(III) and slowly released via alkaline hydrolysis where it was further oxidized by I_2 or was present and slowly oxidized by I_2. Pozhidaev and Gorbachev [Russ. J. Phys. Chem. 1597 (1964)] studied the oxidation products of tartaric acid by Fenton's reagent. One of the products identified was dihydroxy-maleic acid. Lundblad(Arhiv. Kemi. Mineral. Geol. 25A, 1947; C. A. 42; 7249.) has reported upon the chemistry of dihydroxy-maleic acid and I_2. Iodine oxidizes dihydroxymaleic acid to dihydroxytartaric acid among other things. Further, dihydroxymaleic acid is rather unstable and rapidly loses one carboxyl group.

A modified version of the original procedure was then adopted. After the completion of the Cr(VI)-As(III) reaction in tartaric acid, a sample was treated with sodium borate and heated to boiling. The solution was cooled immediately to about

5 C^O and titrated with I$_2$. End points were sharp and stoichio-
metries were reproducible. It is these results which are tabulated
in Tables II and III.

These results clearly indicate the presence of an induced
oxidation of tartaric acid. The fact that as the tartaric acid
is increased at fixed As(III), the $\frac{As(III)}{Cr(VI)}$ ratio becomes
constant suggests that the reaction is not a typical chain
reaction. The decrease is in the direction expected. The
$\frac{As(III)}{Cr(VI)}$ ratio at high tartaric acid and low As(III) leads
to different results which may be due to experimental difficulties
in accurately determining the unreacted As(III) or perhaps
incomplete reaction.

The significance of the stoichiometric analysis is simply
that while the reaction is quite complex and accelerated by
tartrate it does not appear to be a chain reaction.

B. Kinetics of the Cr(VI)-As(III) Reaction in the Presence
of Tartrate.

Some features of the kinetics are demonstrated in Figs.
2,3,4, and 5 and Tables (IV), (V) and (VI). The general
characteristics of these data in summary are (1) the catalysis
is markedly pH dependent paralleling the concentration of mono
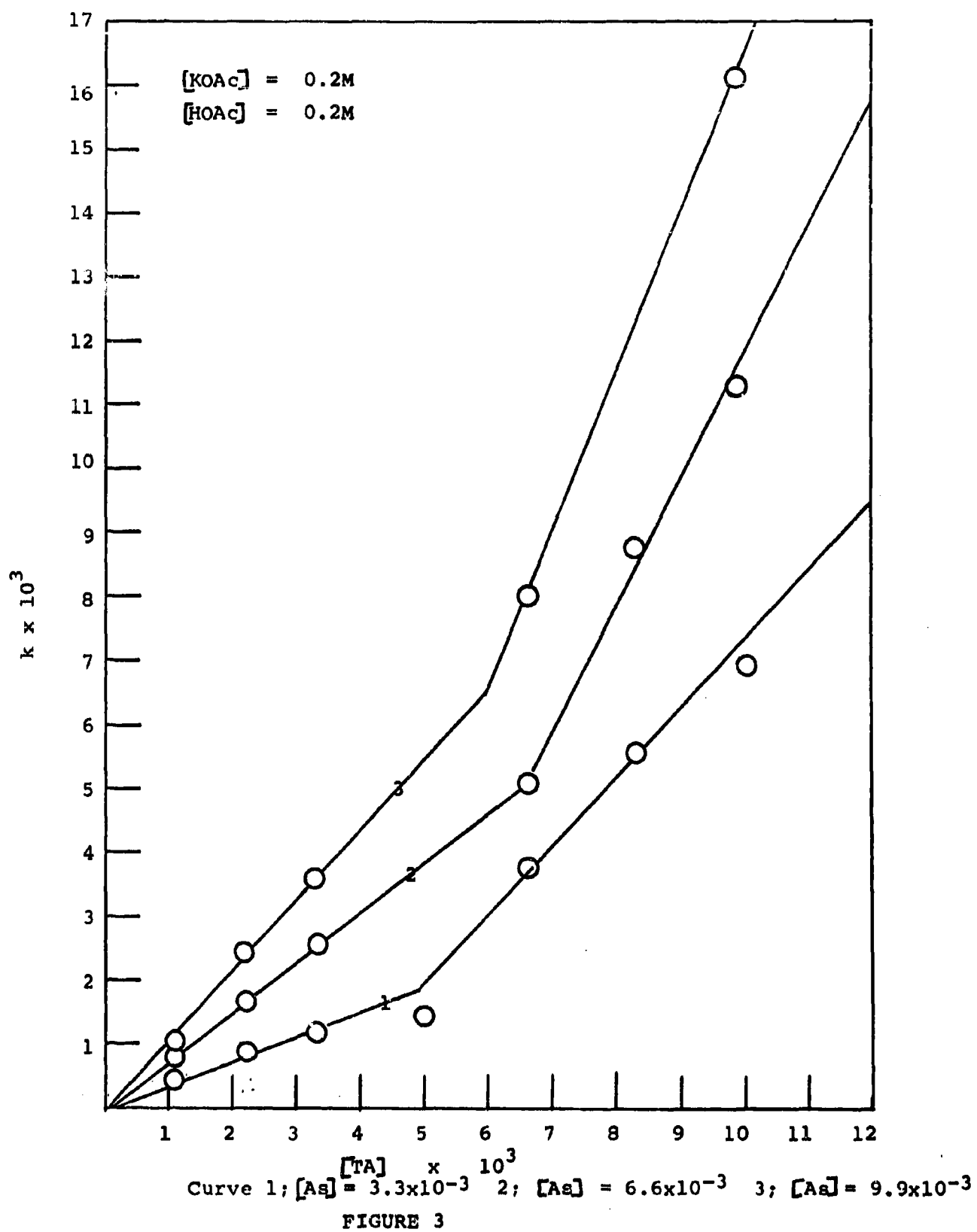acid tartrate in a general way;

(2) Plots of rates of the reaction as a function of tartaric
acid at fixed As(III) all show two slopes, indicating quite
complex behavior.

3) At fixed tartaric acid with variable As(III), all
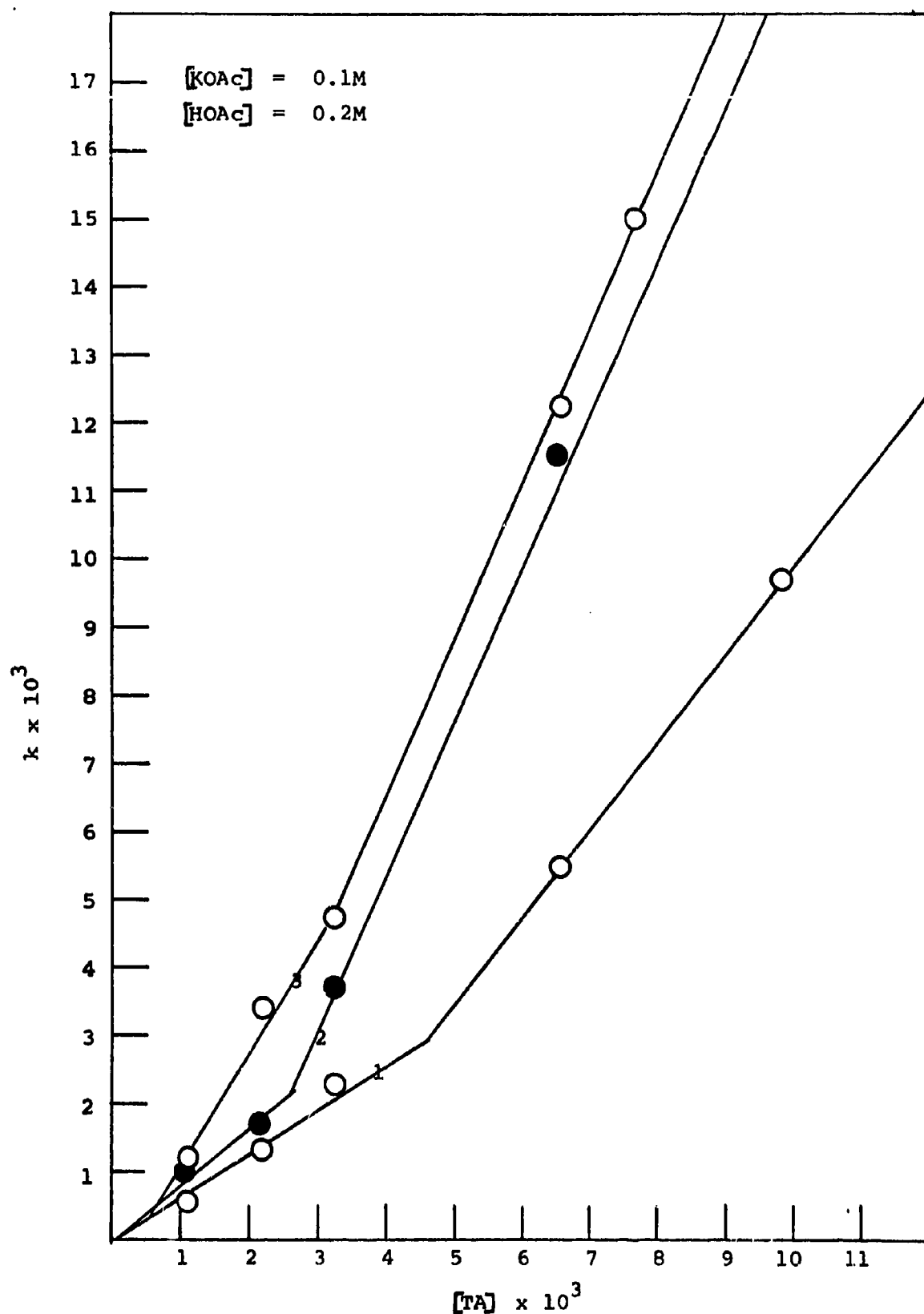
Curve 1; [As] = 3.3x10⁻³; 2; [As] = 6x10⁻³   3; [As] = 9.9x10³
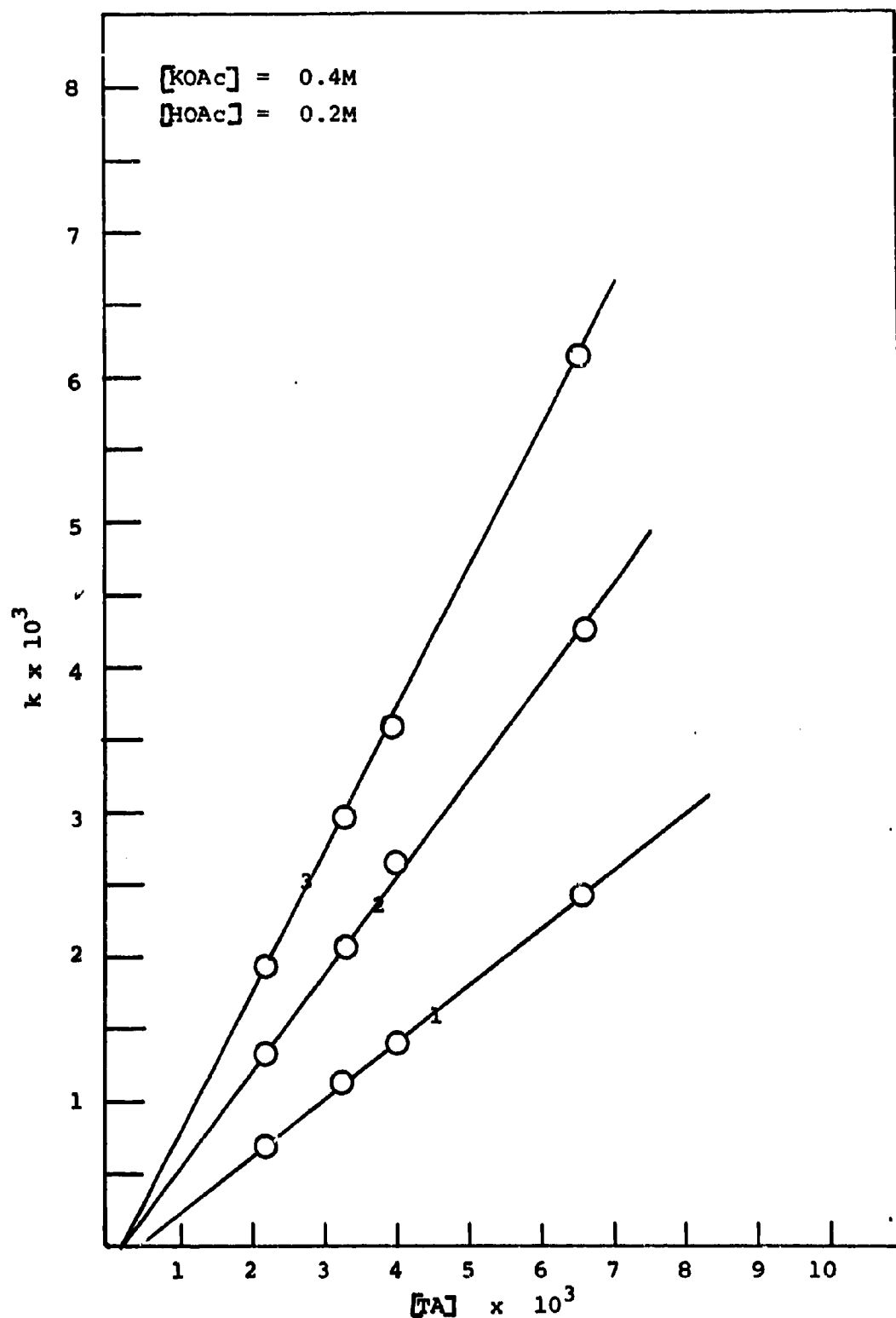
FIGURE 2

Curve 1; $[As] = 3.3 \times 10^{-3}$ 2; $[As] = 6.6 \times 10^{-3}$ 3; $[As] = 9.9 \times 10^{-3}$

FIGURE 3

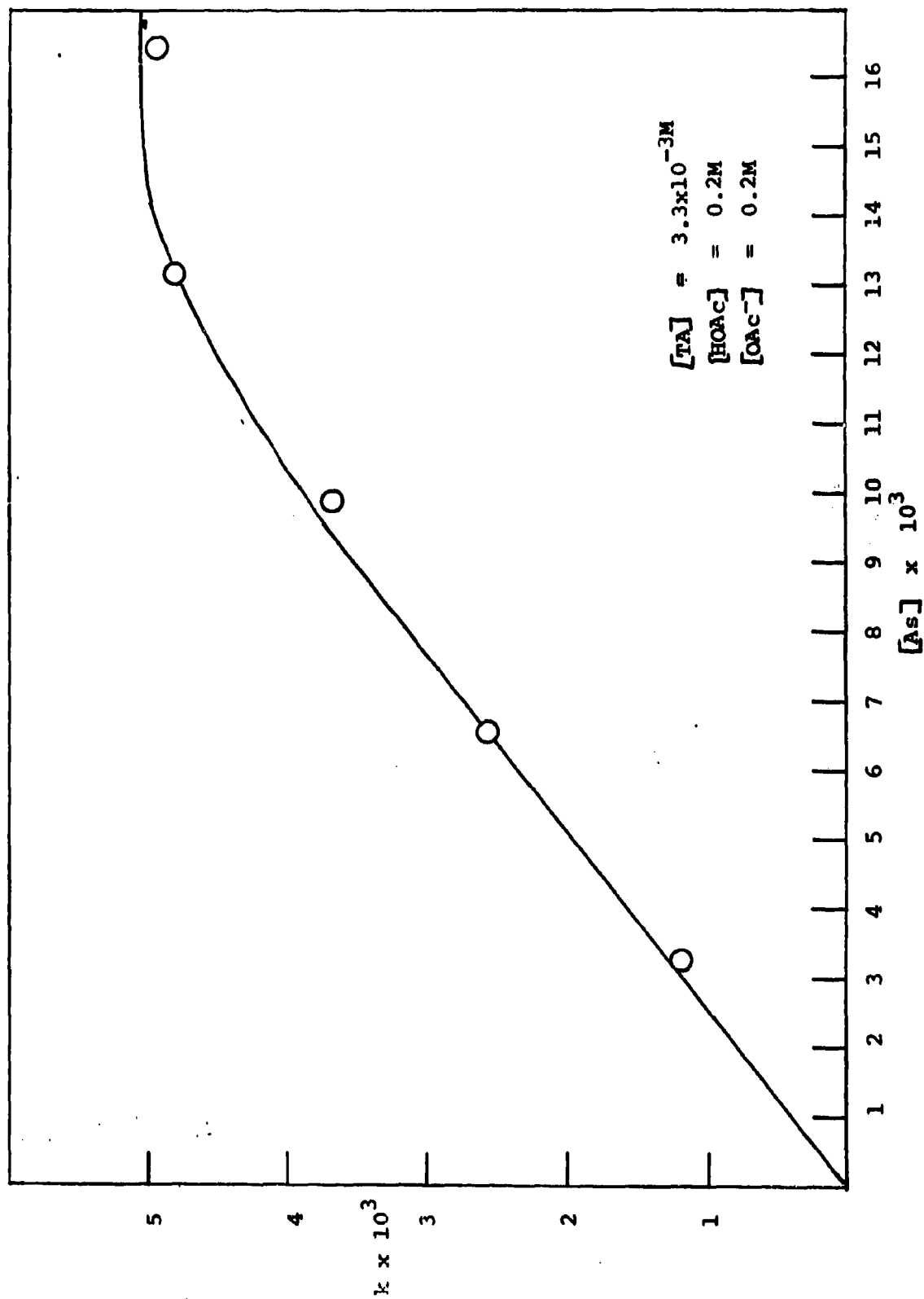Curve 1; [As] = 3.3x10^{-3}   2; [As] = 6.6x10^{-3}   3; [As] = 9.9x10^{-3}

FIGURE 4

$[TA]$ = $3.3 \times 10^{-3}M$
$[HOAc]$ = $0.2M$
$[OAc^-]$ = $0.2M$

$[As] \times 10^3$

$k \times 10^3$

FIGURE 5

Table II

As/Cr Ratio as a Function of Tartaric Acid
(0.2M KOAc, 0.2M HOAc, 1.3M KNO_3)

Initial $[As(III)] = 5 \times 10^{-3} M$
Initial $[Cr(VI)] = 2 \times 10^{-3} M$

$[Tartaric\ Acid]$	$\dfrac{[As(III)]}{[Cr(VI)]}$
$1 \times 10^{-3} M$	0.71
$2 \times 10^{-3} M$	0.43
$5 \times 10^{-3} M$	0.41
$10 \times 10^{-3} M$	0.42
$20 \times 10^{-3} M$	0.43

Table III

As/Cr Ratio at Fixed Tartaric Acid
(0.2M KOAc, 0.2M HOAc, 1.3M KNO_3)

Initial $[Cr(VI)] = 2 \times 10^{-3} M$
Initial $[Tartaric\ Acid] = 10 \times 10^{-3} M$

$[As(III)]$	$\dfrac{[As(III)]}{[Cr(VI)]}$
$1 \times 10^{-3} M$	0.342
$2 \times 10^{-3} M$	0.39
$4 \times 10^{-3} M$	0.39
$5 \times 10^{-3} M$	0.42
$6 \times 10^{-3} M$	0.425
$7 \times 10^{-3} M$	0.475
$10 \times 10^{-3} M$	0.475

Table IV

Effect of Tartaric Acid on Cr(VI) Disappearance in 0.1M KOAc - 0.2M HOAc Buffers.

$[As(III)] \times 10^3$	$[TA] \times 10^3$	$k \times 10^3$	pH
3.3	1.1	.594	4.315
3.3	2.2	1.32	4.305
3.3	3.3	2.29	4.300
3.3	6	4.35	4.297
	6.6	5.52	4.200
	9.9	9.7J	4.155
	13.2	16.81	4.115
	16.5	23.8	4.11
6.6	1.1	1.02	4.315
6.6	2.2	2.67	4.255
6.6	3.3	3.74	4.260
6.6	6.6	11.6	4.215
6.6	9.9	19.2	4.125
9.9	1.1	1.18	4.310
9.9	2.2	3.45	4.276
9.9	3.3	4.71	4.225
9.9	6.6	12.25	4.207
9.9	7.7	15.0	4.262
9.9	9.9	25.1	4.150
9.9	9.9	23.6	4.150

$T = 25^{\circ}C$, $\mu = 1.5$ adjusted with KNO_3.

Table V

Effect of Tartaric Acid on Cr(VI) Disappearance
in 0.2M KOAc-0.2M HOAc Buffers

$[As(III)] \times 10^3$	$[TA] \times 10^3$	$k \times 10^4$	pH
2.0	1	3.06	4.619
2.0	1	3.27	4.615
2.0	2	6.49	4.615
3.3	1.1	4.61	4.615
3.3	2.2	9.21	4.572
3.3	3.3	11.7	4.65
3.3	5.0	14.0	4.610
3.3	6.6	37.8	4.572
3.3	8.3	55.9	4.555
3.3	8.3	55.5	4.540
3.3	10.0	69.8	
3.3	12.0	95.2	4.552
3.3	13.2	105	4.473
3.3	13.2	103	4.60
3.3	16.5	149	4.440
3.3	16.5	149	4.668
6.6	1.1	7.69	4.620
6.6	2.2	16.8	4.625
6.6	3.3	25.6	4.630
6.6	6.6	50.7	4.579
6.6	8.3	87.5	4.532
6.6	9.9	113	4.658(a)
	13.2	172	4.470
	13.2	165	4.645(a)
9.9	1.1	10.5	4.538
9.9	2.2	24.3	4.525
9.9	3.3	36.6	4.618
9.9	3.3	35.6	4.522
9.9	6.6	80.7	4.495
9.9	9.9	162.0	4.435
13.2	3.3	48.4	4.612
16.5	3.3	49.4	4.610

a) pH adjusted prior to run.

T = 25°C, μ = 1.5 adjusted with KNO_3.

Table VI

Effect of Tartaric Acid on Cr(VI) Disappearance
in 0.4M KOAc-0.2M HOAc Buffers

$[As(III)] \times 10^3$	$[TA] \times 10^3$	$k \times 10^4$	pH
2.0	2.2	4.51	5.069
2.0	3.3	7.55	5.057
2.0	4.0	9.21	5.039
2.0	6.0	16.4	5.040
3.3	2.2	7.02	5.060
	3.3	11.2	5.072
	4.0	14.0	5.081
	6.6	24.3	5.030
4.0	2.2	8.57	5.069
	3.3	14.0	
	4.0	16.9	5.048
	6.6	29.7	5.022
6.6	2.2	13.4	5.058
	3.3	20.5	5.055
	4.0	26.5	5.033
	6.6	42.6	5.022
9.9	2.2	19.4	5.082
	3.3	29.6	5.023
	4.0	35.9	5.078
	6.6	61.5	5.020

$T = 25^{\circ}C$, $\mu = 1.5$ adjusted with KNO_3.

reactions studied show a "saturation effect" (rate becomes independent of As(III) at high As(III) concentrations). Plots of $\frac{1}{k}$ vs $\frac{1}{[As(III)]}$ are linear but the slopes and intercepts are complex functions of both the tartaric acid concentration and pH.

4) There is definitive evidence that some tartaric acid is consumed _via_ coordination to the Cr(III) product. Due to the extreme inertness of Cr(III) with respect to substitution reactions it seems clear that the tartrate is incorporated in the Cr(V) or Cr(IV) stages. Similar incorporation reactions have been demonstrated by Beck and Bardi [Acta Chim. Hung., 29, 283 (1961)] and Rikens and Reilley [Anal. Chem., 34, 1707 (1962)].

Many quantitative correlations have been attempted but without significant success. A major source of the difficulty is the appearance of two slopes. Such curves have been obtained in other systems containing complexing agents, notably the work of Margerum on EDTA complexes where some EDTA reacts with metal ions present in the system and produces a curve very similar to a titration curve. Our results however do not appear to be explicable on that basis. Efforts to establish association between As(III) and tartaric acid were not successful. In most instances, the best fit intercept at zero rate for the tartaric acid plots was not zero but corresponded to approximately 3×10^{-4} M tartrate. This occurs in virtually all systems and seems definitely related to the Cr(III) expected at the end, namely 1.2×10^{-4} M.

The other inflection point is much harder to define but appears
to be related to the As(III). A reasonable, but not quatitative,
mechanism for the effect of tartaric acid can be written followir
Beck and Bardi.

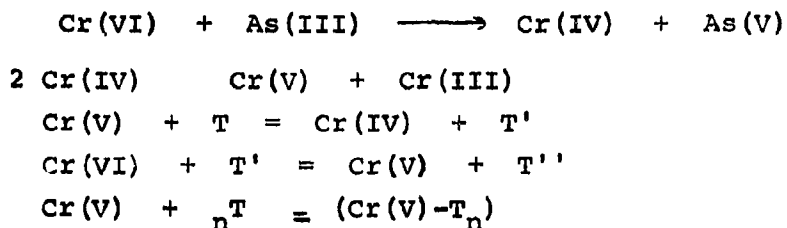The primary reaction produces Cr(IV) _via_ the overall
reaction

$$Cr(VI) + As(III) = Cr(IV) + As(V)$$
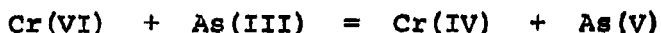
The fate of the Cr(IV) is not normally detectable but
the following reactions may account for its disappearance:

either $2Cr(IV) \longrightarrow Cr(V) + Cr(III)$
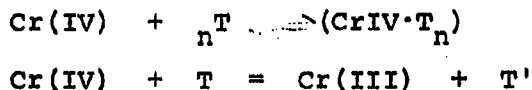
or $Cr(IV) + Cr(VI) = 2Cr(V)$.
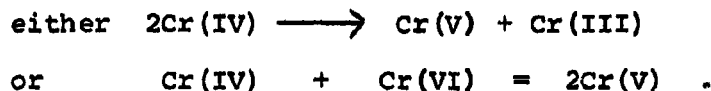
Of these the first with a calculated K of approximately 47 is
the more likely according to Wetton and Higginson [J. Chem.
Soc., 5890 (1965)]. In the presence of an oxidizable substrate
Cr(V) may oxidize either As(III) or the substrate, or Cr(IV)
may oxidize the substrate. The oxidation of tartaric acid by
either Cr(IV) or Cr(VI) would produce organic products capable
of further oxidation. At high tartrate Cr(IV) may be complexed
by the tartrate leading to incorporation rather than destruction.
It is possible that Cr(IV) might oxidize rather than coordinate
and that this accounts for the rate enhancement at low tartrate.
However it is clear that coordination of Cr(V) without any
oxidation what so ever would not alter the stoichiometry if all
Cr(V) was reduced by As(III) and indeed the rate of disappearance

of Cr(VI) would be unaffected.

These observations lead to a mechanism of this form:

$$Cr(VI) + As(III) \longrightarrow Cr(IV) + As(V)$$

$$2\ Cr(IV) \quad Cr(V) + Cr(III)$$
$$Cr(V) + T = Cr(IV) + T'$$
$$Cr(VI) + T' = Cr(V) + T''$$
$$Cr(V) + {}_nT = (Cr(V)-T_n)$$

At high tartrate

$$Cr(IV) + {}_nT \longrightarrow (CrIV \cdot T_n)$$
$$Cr(IV) + T = Cr(III) + T'$$

In either case Cr(VI) is reduced by oxidizable organic materials produced by the induced oxidation of tartaric acid.

Since no detailed study of Cr(III)-tartaric acid complexes seems to be available it was impossible to establish the nature of the complex formed or whether a variety of complexes was formed as the tartaric acid increased.

Experimentally, not enough tartrate is either incorporated or oxidized to alter the effective concentration of tartrate during one run. Further, product analysis of the actual organic species produced by the induced reaction could not be achieved successfully because of the very low concentrations.

Work is now in progress on the effect of oxalate with these initial results: oxalate incorporates and catalyzes the Cr(VI)-As(III) without alteration of the stoichiometry.

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13. ABSTRACT

The kinetics of the Cr(VI)-As(III) reaction have been investigated in $H_2PO_4^-$ - HPO_4^- buffers. Complex kinetics have been obtained. The rate law found is first order in total Cr(VI) and As(III) with a complex dependence upon buffer composition. The data point to the reaction proceeding via two activated complexes, $\left[H_2PO_4^- \cdot HCrO_4^- \cdot As(III)\right]$ and $\left[HPO_4^= \cdot HCrO_4^- \cdot As(III)\right]$.

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